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In Situ Bioremediation of Contaminated Unsaturated Subsurface Soils

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Introduction

An emerging technology for the remediation of unsaturated subsurface soils involves the use of microorganisms to degrade contaminants which are present in such soils. Understanding the processes which drive in situ bioremediation, as well as the effectiveness and efficiency of the utilization of these systems, are issues which have been identified by the Regional Superfund Engineering Forum as concerns of Superfund decision makers.

The Regional Superfund Engineering Forum is a group of EPA professionals, representing EPA's Regional Superfund Offices, committed to the identification and resolution of engineering issues impacting the remediation of Superfund sites. The Forum is supported by and advises the Superfund Technical Support Project.

Although in situ bioremediation has been used for a number of years in the restoration of ground water contaminated by petroleum hydrocarbons, it has only been in recent years that in situ systems have been directed toward contaminants in unsaturated subsurface soils. Research has contributed greatly to understanding the biotic, chemical, and hydrologic parameters which contribute to or restrict the application of in situ bioremediation and has been successful at a number of locations in demonstrating its effectiveness at field scale.

This document is one in a series of engineering issue papers which have been prepared in response to needs expressed by the Engineering Forum. It is based on findings from the research community in concert with experience gained at sites undergoing remediation. The intent of the document is to provide an overview of the factors involved in in situ bioremediation, outline the types of information required in the application of such systems, and point out the advantages and limitations of this technology.

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Background

Bioremediation of contaminated surface soils using in situ systems, prepared bed, and above-ground bioreactors, has been previously addressed with regard to characterization, environmental processes and variables, and field-scale applications (Sims et al.,1989). This paper will address processes which are currently being utilized or are in development to treat contaminated unsaturated subsurface soils in place.

In situ biological remediation of subsurface soils contaminated with organic chemicals is an alternative treatment technology that, in certain cases, can meet the goal of achieving a permanent cleanup at hazardous waste sites. Use of such alternatives is encouraged by the U.S. Environmental Protection Agency (U.S. EPA) for implementing the requirements of the Superfund Amendments and Reauthorization Act (SARA) of 1986. Bioremediation of subsurface soils is consistent with the philosophical thrust of SARA, for it involves use of naturally occurring microorganisms to degrade and/or detoxify hazardous constituents in the soil to protect public health and the environment. Use of in situ subsurface bioremediation

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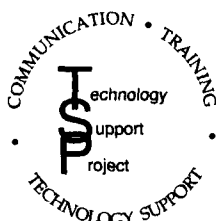
techniques in conjunction with chemical and physical treatment processes, i.e., "treatment trains," is an effective means for comprehensive site-specific remediation (Ross et al., 1988; Sims, 1990). For instance, bioremediation may be utilized to lower the concentration of organic contaminants in a soil matrix before stabilization or solidification is used as a remedial alternative for metals.

Bioremediation has been shown effective in reducing the overall mass of a variety of organic contaminants. Full scale systems have been utilized to remediate soil contaminated with both crude and refined petroleum hydrocarbons (i.e., diesel fuel, gasoline), creosote, and pentachlorophenol. To date, it has not been shown effective at removing highly structured, highly insoluble compounds such as polychlorinated biphenyls and dioxins.

For the purposes of this document, subsurface soil refers to unsaturated soil within the vadose zone at depths greater than three feet below the land surface. The vadose zone extends from the ground surface to the upper surface of the principal water-bearing formation (Everett et al., 1982). The vadose zone usually consists of three to six feet of topsoil (weathered geological materials) which gradually merges with deeper underlying earth materials such as depositional or transported clays or sands. In this zone, water primarily coexists with air, though saturated regions may occur. Perched water tables may develop at interfaces of layers (soils having different textures) of soil having less hydraulic conductivity. Prolonged infiltration also may result in transient saturated conditions. In some regions, the entire vadose zone may be hundreds of feet thick and the travel time of constituents to ground water can be hundreds or thousands of years. Other regions may be underlain by shallow potable aquifers that are especially susceptible to contamination due to short transport times and reduced potential for pollutant attenuation by soil materials and processes.

This document addresses specific environmental processes, factors, and data requirements for characterizing and evaluating the application of subsurface in situ bioremediation, and describes selected field-scale applications of recovery and delivery systems to enhance in situ subsurface soil bioremediation.

Overview: In Situ Subsurface Microbial Processes and Controlling Environmental Factors

The rate and extent of biodegradation of organic chemicals during subsurface in situ bioremediation are influenced by several site-specific factors. These include type and activity of microbial populations; chemical environmental factors; bioavailability of the target chemical(s) and other substrates required for co-metabolism, i.e., electron donor; mass transport of moisture, nutrients, and oxygen (the terminal electron acceptor in aerobic metabolism); toxicity; and stratigraphy, heterogeneity, and geochemistry of the surface or subsurface environment. A detailed discussion of the impact of these and other factors on bioremediation can be found in "Transport and Fate of Contaminants in the Subsurface" (EPA/625/4-89/019) and "Bioremediation of Contaminated Surface Soils" (EPA/600/9-89/073).

Microbial Populations

Successful in situ bioremediation depends on the presence of appropriate microbial populations which can be stimulated to degrade contaminants of concern by modifying or otherwise managing environmental conditions at a site. Results of microbial characterization of deep subsurface materials have indicated that: (1) microorganisms are present at populations sufficient to change the chemistry of the environment when stimulated; (2) the microbial communities are diverse and carry out a wide range of chemical transformations; (3) a majority (>95%) of the microbes are chemotrophic bacteria that degrade organic chemicals to obtain energy; and (4) environmental characteristics identified previously (oxygen concentration, nutrient status, moisture content) are important in influencing microbial activity and degradation patterns (Fliermans and Hazen, 1990).

Microbial communities in the subsurface are diverse and adaptable. Microbial populations at older sites are usually acclimated to the contaminants of concern. Therefore, levels of critical nutrients or electron acceptors, toxicity, and adverse environmental conditions most often are the major factors which limit the extent and rate of in situ bioremediation.

Critical Environmental Conditions

There are several environmental conditions that affect activity of soil microorganisms. These factors, along with individual soil and waste characteristics, all interact to affect microbial activity at specific contaminated sites. Many of these conditions can be managed to enhance biodegradation of organic constituents in subsurface soils. Optimum ranges for the most critical of these factors are presented in Table 1.

Water content of soil is an important factor which regulates microbial activity. Soil water serves as the transport medium through which many nutrients and organic constituents diffuse to the microbial cell, and through which metabolic waste products are removed. Soil water also affects soil aeration status, nature and amount of soluble materials, osmotic pressure, pH of the soil solution, and unsaturated hydraulic conductivity of the soil (Paul and Clark, 1989). The water content of deeper subsurface soils may vary greatly. Unsaturated soil samples have been obtained even from cores collected below the water table in deep subsurface environments, and the low water content was shown to adversely affect microbial activity (Kieft et al., 1990).

Biodegradation rates often depend on the rate at which terminal electron acceptors can be supplied. A large fraction of the microbial population within soils are aerobes which use oxygen as the terminal electron acceptor. Oxygen can be easily depleted in subsurface soils where there is an oxygen demand due to plant root respiration or due to normal

Table 1. Critical environmental factors for microbial activity (Sims et al., 1984; Huddleston et al., 1986; Rochkind and Blackburn, 1986; Paul and Clark, 1989)

Environmental Factor	Optimum Levels
Available soil water	25%-85% of water holding capacity; -0.01 MPa
Oxygen	Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimum air-filled pore space of 10%; Anaerobic metabolism: O_2 concentrations <1%
Redox potential	Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts
pH	5.5-8.5
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth Suggested C:N:P ratio of 100:10:1
Temperature	15°C-45°C (Mesophiles)

microbial activity throughout the depth of the unsaturated zone. Oxygen levels tend to decrease in soils having high clay and organic matter content. Clayey soils tend to retain higher moisture content, which restricts oxygen diffusion, while organic matter may increase microbial activity and deplete available oxygen. Under these circumstances, oxygen may be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil may become anoxic.

Facultative anaerobic organisms (which can use oxygen or alternative electron acceptors such as nitrate or sulfate in the absence of oxygen) and obligate anaerobic organisms then become the dominant populations under such conditions. The sequence of use of various electron acceptors is determined by the redox potential and the electron affinity of the electron acceptors present (Zehnder and Stumm, 1988). The potential of alternative electron acceptors has been evaluated with nitrate at field scale for contaminants (including benzene, toluene, and xylene) in an aquifer environment (Hutchins et al., 1991).

Redox potential also affects metabolic processes in subsurface microbial populations (Paul and Clark, 1989). Redox potential provides a measurement of electron density and is related to the oxygen status of a subsurface soil. As oxygen is removed and a system becomes more reduced, there is a corresponding increase in electron density, resulting progressively in an increased negative potential.

Soil pH affects growth and activity of subsurface soil microorganisms. Fungi are generally more tolerant of acidic

soil conditions (below pH 5) than bacteria. Solubility of phosphorus, a critical nutrient in biological systems, is maximized at a pH value of 6.5. A specific contaminated soil system may require management of soil pH to achieve levels that maximize microbial activity. Control of pH to enhance microbial activity may also aid in the immobilization of hazardous metals in a subsurface soil system (a pH level greater than 6 is recommended to minimize metal transport). Subsurface soil pH may be managed through addition of an aqueous phase containing pH adjusting chemicals through gravity delivery systems such as infiltration galleries or surface irrigation systems.

Microbial metabolism and growth depends upon adequate supplies of essential macro- and micro-nutrients. Critical nutrients such as nitrogen and phosphorous must be present and available to microorganisms in: (1) usable form; (2) appropriate concentrations; and (3) proper ratios (Dragun, 1988). If wastes are high in carbon (C), and low in nitrogen (N) and phosphorus (P), biodegradation will cease when available N and P are depleted. Therefore, fertilization of subsurface soils may be required as a management technique to enhance microbial degradation.

Soil temperature affects microbial growth and metabolic activity. Biodegradation rates decrease as temperature drops and essentially cease at temperatures below 0° C. While surface soils exhibit both diurnal and seasonal variations in temperature, changes of temperature decrease with depth. Generally, only the top 30 feet of the subsurface profile are affected by seasonal variations in temperature; temperature is generally constant and corresponds to the

mean annual air temperature of the locality (Kuznetsov et al., 1963; Matthess, 1982). In the United States, temperatures in this zone range from 3°C to 25° C (Dunlap and McNabb, 1973). Due to the high specific heat of water, wet soils are less subject to larger diurnal changes than dry soils (Paul and Clark, 1989).

Bioavailability is a general term which refers to the accessibility of contaminants by degrading populations. There are two major components involved: (1) a physical aspect related to phase distribution and mass transfer limitations of the contaminant, and (2) a physiological aspect related to the suitability of the contaminant as a substrate.

Major factors which affect bioavailability include water solubility and sorption. Target chemicals may occur in one or more of the four phases comprising the subsurface soil environment: (1) soil solids, including organic matter and inorganic sand, silt, and clay particles; (2) soil water; (3) soil gas; and (4) often a nonaqueous phase liquid (NAPL) . In general, chemicals that distribute to the water phase (more soluble) are more bioavailable than chemicals that either sorb strongly to solid phases or occur in a NAPL phase. NAPLs are generally degraded from the water:NAPL interface inward since the aqueous phase contains nutrients, oxygen, and moisture required for microbial life processes. The bioavailability of a NAPL phase may be increased by increasing the surface area to volume ratio of NAPL elements. This increases mass transfer of nutrients, moisture, and oxygen; and decreases toxicity by decreasing interfacial concentrations (Symons and Sims, 1988). Substrate chemicals in the gas phase have also been found to be bioavailable (Dupont et al., 1991; Miller et al., 1991). Generally, chemicals that are highly sorbed, such as high molecular weight PAHs present in creosote, petroleum, and manufactured town gas plant wastes, are found to be degraded at slower rates than chemicals that are only slightly sorbed. Since the majority of the mass of target constituents at many contaminated sites is associated with NAPL and/or solid phases, these represent the greatest challenge with regard to in situ bioremediation.

Bioavailability is also a function of the biodegradability of the target chemical, i.e., whether it acts as a substrate, cosubstrate, or is recalcitrant. The target chemical may be physically available (i.e., water soluble and/or not sorbed to solids) but not useful as a metabolic substrate. Contaminants of concern may not be the dominant organic substrate in a system. When the target chemical cannot serve as a substrate (source of carbon and energy) for microorganisms, but is oxidized in the presence of a substrate already present or added to the subsurface, the process is referred to as cooxidation and the target chemical is defined as the cosubstrate (Keck et al., 1989; Sims et al.,1989). Cooxidation processes are important for the biodegradation of high molecular weight polycyclic aromatic hydrocarbons (PAHs), and some chlorinated solvents, including trichloroethylene (TCE). Contaminants with complex molecular structures or high degrees of toxicity may not be degradable, and may persist or be recalcitrant under aerobic conditions. Examples of recalcitrant compounds include highly oxidized halogenated compounds such as polychlorinated biphenyls (PCBs), pesticides such as toxaphene, and dioxin contaminants present in wood-preserving wastes.

The toxicity of the environment may be reduced by decreasing the concentration of a toxic waste (e.g., creosote) or chemical (e.g., pentachlorophenol) within one or more subsurface phases. Concentrations of toxic chemicals in the gas phase may be reduced through soil vacuum extraction; in the water phase through soil flushing; in the NAPL phase through soil flushing with water containing viscosifiers, or with solvents or surfactants; and in the soil solid phase by inducing partitioning of contaminants from solid to fluid phases. All mobile phases in the subsurface have potential for escape; therefore, containment strategies are often necessary while the constituents within the phase are biodegraded.

Heterogeneity of the subsurface environment limits the rate and extent of in situ bioremediation. Restrictive layers (e.g., clay lenses), although more resistant to contamination, are also more difficult to remediate due to poor permeability and low rates of diffusion. Clay soils have larger porosities than silty or sandy soils and therefore larger storage capacities for contaminants, but have greater resistance to fluid flow including aqueous, gas, and NAPL phases. Also clay layers with poor hydraulic conductivity are less permeable to nutrients and oxygen. In sites that have substantial clay and silt deposits, more permeable soils will become preferential conduits for remedial fluids, and the clay/silt deposits will require much longer time frames for remediation. For example, heterogeneity of the subsurface with respect to soil layering and chemical parameters at a gas works site in the United Kingdom presented constraints on the feasibility of utilizing in situ bioremediation (Thomas et al., 1991).

Enhancement of In Situ Subsurface Bioremediation

The method of enhancing in situ bioremediation efforts depends on the four phases in which contaminants can occur, heterogeneity of subsurface matrix, and the types of delivery and recovery systems utilized. Removing limiting or controlling factors and establishing favorable conditions are the primary goals of recovery and/or delivery systems. Enhancement may be achieved by increasing bioavailability; reducing toxicity; increasing delivery of moisture, nutrients, and oxygen; and/or by introducing substrates that stimulate indigenous microbial degradative activity.

A variety of strategies may be implemented to maximize biodegradation activity in contaminated subsurface soils. The success of in situ bioremediation efforts is often determined by the effectiveness of the recovery and delivery systems used to remove major sources of contaminants and to transport nutrients and electron acceptors to the location of the remaining contaminants. Establishing optimum levels of essential nutrients and electron acceptors at specific subsurface locations is often driven by physical limitations of

the subsurface matrix on transport of fluids (liquids or gases) used to deliver these amendments. Overcoming these limitations is the primary goal of a delivery system, and the development of adequate delivery technologies continues to be the major challenge of in situ bioremediation. A summary of delivery and recovery techniques commonly used to manage subsurface remediation is provided in Table 2.

Making the Saturated Zone Unsaturated

Advantages of Unsaturated Systems

Because hydraulic conductivity is a function of soil moisture content, changing a saturated soil into an unsaturated soil greatly reduces the hydraulic conductivity and therefore the downward transport of chemicals in the water phase to the ground water . Also, because oxygen diffuses through air 10,000 times faster than through water, an unsaturated environment may be maintained in an aerobic condition more easily than a saturated environment in the presence of oxygen-demanding chemicals (Table 3). Soil pore space that contains a gas phase also allows removal of volatile contaminants (via soil vacuum extraction) in a direction that is away from the ground water. Therefore, management of a site to change the saturated zone to an unsaturated condition may reduce potential for ground-water contamination as well as enha:·ced oxygen delivery to stimulate in situ biodegradation.

Physical Containment

There are a variety of approaches to establishing and maintaining dewatered conditions. In order to adequately dewater the subsurface, it is often necessary to physically isolate the treatment zone. Impermeable subsurface barriers can prevent the migration of ground water by preventing uncontaminated water from entering the contaminated site and stopping contaminated water from leaving. Extraction systems or drains must then be used to remove the ground water to create an unsaturated zone.

Commonly used barriers include slurry walls, grout curtains, and sheet piling cutoff walls to retard the flow of water under and through a site (Devinny et al., 1990).

Ground-Water Removal

Ground-water removal can be accomplished by hydraulic pumping and/or drainage trenches. Hydraulic pumping using a well-point system is one such technique (Devinny et al., 1990) using short lengths of plastic or Teflon well screen placed in the saturated zone.

Ground water can also be removed using subsurface drains or drainage ditches. Subsurface drains are constructed by excavating a trench to the desired depth, partially backfilling the trench with highly permeable sand or gravel, placing a plastic or ceramic drain tile in the sand and gravel bed, and completing the backfilling (Devinny et al., 1990).

Drainage ditches or surface drains are similar to subsurface drains except that no collection pipes or tiles and backfills are used. They may be used at sites underlain by poorly permeable soils (Devinny et al., 1990).

Recovery and Delivery Technologies for Subsurface Bioremediation

Recovery and delivery technologies are those that facilitate transport of materials either out of or into the subsurface (Murdoch et al., 1990). Recovery technologies are primarily utilized for contaminant source reduction. High levels of contamination present as either trapped residuals or NAPLs can severely limit success of bioremediation attempts. Therefore, removal of as much of this initial contaminant mass as possible is a prerequisite to in situ bioremediation efforts.

Specific recovery and delivery technologies for enhancing in situ bioremediation of subsurface soils are identified in Table 2. Each identified technology is discussed below with regard to its applications and limitations, and current status.

Recovery Technologies

The principal recovery technologies used for subsurface remediation depend on the ability to move fluids. Also involved is the ability to move contaminants by altering their solubility or sorption characteristics (Murdoch et al., 1990). These techniques are used to move materials from the subsurface soil environment in order to enhance in situ bioremediation by addressing one or more limiting factors identified in Tables 1 and 2, including: soil vacuum extraction, soil flushing, steam stripping, and radio frequency heating.

Soil vacuum extraction

Soil vacuum extraction (SVE) (also referred to as subsurface or forced air venting, in situ air stripping, or soil vapor extraction) involves the removal of contaminants carried in the soil gas phase by reduction of the vapor pressure within the soil pores by applying a vacuum. As clean air is drawn through the soil, the contaminants are removed. This process is driven by concentration differences between solid, aqueous, and NAPL phases and the clean air that is introduced through the soil vacuum extraction process.

Vacuum extraction is most applicable to sites contaminated with highly volatile compounds, such as those associated with gasoline and solvents (e.g., perchloroethylene, trichloroethylene, dichloroethylene, trichloroethane, benzene, toluene, ethylbenzene, and xylene).

Important soil characteristics that should be measured or estimated to determine the feasibility of vacuum extraction at a specific site include physical factors that control the rate and extent of air flow through contaminated soil, and chemical factors that determine the amount of contaminant that partitions from soil to air. These factors include: bulk density (weight per volume); total porosity (void spaces

Table 2. Management strategies for addressing factors limiting in situ bioremediation of subsurface soils

Limiting Factor	Management Response	Delivery or Recovery Technique
Bioavailability limited due to NAPL	Reduce NAPL mass	Gravity or forced delivery; Soil flushing, Steam stripping, Hydraulic fracturing
Bioavailability limited by sorption or slow mass transport through soil matrix	Reduce sorption, Increase mass transport	Soil flushing, Steam stripping, Hydraulic fracturing
Moisture	Add water or water saturated air	Gravity or forced delivery; Bioventing, Cyclic pumping
Nutrients	Add nutrients in water or as ammonia gas	Gravity or forced delivery; Bioventing, Cyclic pumping
Oxygen/Redox	Add air	Bioventing, Hydraulic fracturing, Cyclic pumping, Radial drilling, Kerfing
Toxicity	Remove chemicals	Soil vacuum extraction, Soil flushing, Steam stripping
pH	Adjust soil pH	Gravity or forced delivery
Temperature	Increase temperature	Radio frequency heating, Steam stripping
Substrate Addition	Add in water or air	Gravity or forced delivery; Bioventing, Hydraulic fracturing
Heterogeneity	Add or withdraw material in more restrictive layers	Cyclic pumping, Hydraulic fracturing, Radial drilling, Kerfing

Table 3. Carrier fluid oxygen supply requirements (Dupont et al., 1991)

Carrier	g Carrier/g O_2
Water	
Air Saturated	110,000
Pure O_2 Saturated	22,000
500 mg/L H_2O_2 (100% Utilization)	2,000
Air (20.0% O_2)	13

between soil grains) and air-filled porosity (that portion of the total porosity filled with air); diffusivity of volatiles (amount of volatiles which move through an area over time); soil moisture content (percentage of void spaces filled with water); air phase permeability (ease with which air moves through soils); texture; structure; mineral content; surface area; temperature; organic carbon content; heterogeneity; depth of air permeable zone; and depth to water table (Metcalf & Eddy, Inc., 1991). Soils at sites where vacuum extraction is used should be fairly homogeneous and have high permeability, porosity, and uniform particle-size distributions (Metcalf & Eddy, Inc., 1991). Soil vapor transport can be severely limited in a soil with high bulk density, high soil water or high NAPL content, low porosity, and low permeability. In heterogeneous soils, air flows preferentially through more permeable zones, leaving less permeable zones untreated.

Contaminant characteristics that affect the feasibility of vacuum extraction include the extent and degree of contamination, vapor pressure, Henry's law constant, aqueous solubility, diffusivity, and partition coefficients. Due to the high solubility of many organic contaminants in NAPL phases, the presence of NAPL in subsurface soil systems

may significantly affect the distribution of the compounds in various phases, and their fate in SVE systems. Specific contaminant and soil conditions that determine the feasibility of vacuum extraction are presented in Table 4.

The efficiency of a vacuum extraction system can be enhanced in several ways. For example, a system of air injection wells can be installed at the perimeter of a contaminated area (Metcalf & Eddy, Inc., 1991) which can be connected to air blowers to force air into the soil or remain open to the atmosphere. Use of air injection wells can result in increased soil air flow rates and a larger area through which clean air can move.

Pulsed pumping may be used to give contaminants time to desorb from solid surfaces, diffuse from restricting layers, and volatilize from residual saturation (NAPL) in the soil pore space. Using pulsed pumping for recovery of contaminants allows a lower volume of air with higher concentrations of contaminants to be recovered.

If ground water is at or near the zone of soil contamination, water table rise may occur due to reduced air pressure near extraction wells (Metcalf & Eddy, Inc, 1991). Ground-water

Table 4. Conditions affecting feasibility of use of vacuum extraction (U.S. EPA, 1990; Metcalf & Eddy, Inc., 1991)

Condition		Favorable	Unfavorable
Contaminant:			
	Dominant form	Vapor phase	Solid or strongly sorbed to soil
	Vapor pressure	>100 mm of mercury	<10 mm of mercury
	Water solubility	<100 mg/l	>1,000 mg/l
	Henry's Law Constant	>0.01 (dimensionless)	<0.01 (dimensionless)
Soil:			
	Temperature	>20°C (usually will require external heading of soils)	<10°C (common in northern climates)
	Air conductivity	>10^{-4} cm/s	<10^{-6} cm/s
	Moisture content	<10% (by volume)	>10% (by volume)
	Composition	Homogeneous	Heterogeneous
	Surface area of soil matrix	<0.1 m^2/g of soil	>1.0 m^2/g of soil
	Depth to ground water	>20 m	<1 m

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pumping may be used to counteract the water table rise, as well as to expose additional contaminated soil that can be treated by vacuum extraction.

Horizontal extraction wells (wells drilled parallel to ground surface) have been used for deep subsurface contamination at the U.S. Department of Energy Savannah River facility to access larger areas of the contaminated site (Hazen,1992). This use of horizontal wells may be a means to reduce costs associated with deep subsurface remediation since only a single hole may be required to access contaminated areas instead of many vertical wells.

The performance of a vacuum extraction system is monitored by system operational characteristics and by treatment efficiency characteristics (Metcalf & Eddy, Inc., 1991). System characteristics include strength of vacuum applied, air flow rate, and contaminant concentrations and moisture content in the vented gas. Wells are used to monitor pressure in the contaminated area. Efficiency of treatment is monitored by soil gas analyses, and soil core analyses to determine residual concentration of contaminants. For more detailed discussions of soil venting evaluation, see "Evaluation of Soil Venting Application" (EPA/540/S-92/004).

Since soil vacuum extraction is an in situ treatment technique that requires only addition of ambient air to the subsurface, it can be applied with little disturbance to existing facilities and operations (Metcalf & Eddy, Inc., 1991). SVE can be used at sites where areas of contamination are large and deep, or when the contamination is beneath a building. The system can be easily modified, depending on additional analytical and subsurface characterization data and/or changing site conditions. Even if vacuum extraction can be implemented at a site, most of the conditions listed in Table 4 must be met, or the cost and time for cleanup will be prohibitive.

The use of SVE at remedial sites has been reviewed by the U.S. EPA (1989a) and classified as a developed technology for remedial applications. It is currently the most commonly used in situ remedial technology (Murdoch et al., 1990). Soil vacuum extraction may be used to reduce toxic concentrations of contaminants to levels which are more conducive to bioremediation. In addition, it will also deliver oxygen to the subsurface which is required by aerobic bacteria.

Soil flushing

In situ soil flushing is used to accelerate movement of contaminants through unsaturated materials by solubilizing, emulsifying, or chemically modifying the contaminants. A treatment solution is applied to the soil and allowed to percolate downward and interact with contaminating chemicals. Contaminants are mobilized by the treatment solution and transported downward to a saturated zone where they are captured in drains or wells and pumped to the surface for recovery, treatment, or disposal (Murdoch et al., 1990). In combination with bioremediation, the flushing solution may be amended with nutrients to enhance biological activity (Metcalf & Eddy, Inc, 1991).

Treatment solutions are delivered to the contaminated zone by using either gravity or forced methods. Forced delivery consists of various pumping techniques. Gravity delivery methods include surface flooding, ponding, spraying, ditching and subsurface infiltration beds and galleries (Amdurer et al., 1986). Barriers, such as slurry walls, may be required to prevent the transport of contaminants away from the site (Metcalf & Eddy, Inc. 1991). A ground-water extraction system must be used to capture the flushing solution and associated contaminants. In some cases, the flushing solution may be treated to remove the contaminants and reused, and in others it may require disposal.

Efficiency of soil flushing is related to two processes: the increase in hydraulic conductivity that accompanies an increase in water content of unsaturated soil, and the selection of treatment solutions with regard to the composition of the contaminants and the contaminated medium. The hydraulic conductivity of soils decreases markedly with decreases in water content; therefore, the flow of liquids through unsaturated soils is extremely slow and the recovery of contaminants by conventional pumping techniques is not possible. With soil flushing, the water content and consequently the hydraulic conductivity of the soil is increased (Murdoch et al., 1990). However, heterogeneities in soil permeability may result in incomplete removal of contaminants.

At sites where water-soluble contaminants are present, water can be used to flush or mobilize the contaminants (Metcalf & Eddy, Inc., 1991). Surfactants can be added to increase the mobility of hydrophobic organic contaminants, such as oils and petroleum. Examples of other flushing solutions include: acidic aqueous solutions (for the removal of metals and basic organic constituents including amines, ether, and anilines), basic solutions, chelating agents, oxidizing agents, and reducing agents. Toxicity of flushing solutions to soil microorganisms should be considered when followed by bioremediation of residual contamination. The flushing solution may change physical and chemical properties of the soil environment that affect bioremediation potential.

The level of treatment that will be achieved is dependent on selection of an appropriate flushing solution, extent and time of contact between the solution and waste constituents, soil partition coefficients of the waste constituents, and the hydraulic conductivity of the soil (Metcalf & Eddy, Inc., 1991). Soil flushing is not applicable to soils with low hydraulic conductivities (e.g., less than 1 ft/day), or for contaminants that are strongly sorbed to the soil (e.g., PCBs, dioxin).

Soil flushing has been classified by the U.S. EPA as a developed technology used for recovery in remedial applications (Murdoch et al., 1990). Although the technology has been tested at field-scale, soil flushing has not yet been used extensively in large-scale clean-up operations. As with SVE systems, soil flushing may be utilized with bioremediation as a coupled technology. Soil flushing may initially be utilized to lower toxic or extreme concentrations of contaminants to a manageable level for biological processes which

may be utilized as a polishing step to remove those contaminants which were not removed through the flushing process. If biological processes are used during or after soil flushing, the compatibility of the soil flushing solution with subsurface bacteria must always be considered.

Delivery Techniques

The major limiting factor to the bioremediation of amenable compounds is the delivery of required nutrients, co-oxidation substrates, electron acceptors or other necessary enhancers of microbial growth. Delivery techniques are used to add required materials to the subsurface environment to enhance in situ bioremediation by addressing one or more limiting factors identified in Tables 1 and 2. A variety of delivery techniques are in use or are being developed (Figures 1-3). These include soil venting, gravity and forced hydraulic delivery, hydraulic fracturing of low permeability zones, radial drilling, and cyclic pumping. Of these, only gravity and forced hydraulic delivery and venting systems are in common use at sites. The other three approaches are still in developmental stages.

In Use: Gravity/Forced Hydraulic Delivery and Bioventing

Gravity and Forced Hydraulic Delivery

Irrigation technologies were among the first utilized for enhancing in situ biodegradation. Gravity methods are used to deliver water and amendments to the contaminated subsurface by applying the solutions directly over the

contaminated area. Applied solutions then percolate downward through the subsurface to contaminated zones. Application methods consist of both surface and subsurface spreading (Amdurer et al., 1986).

Surface application methods include flooding, ponding, ditches, and sprinkler systems. These methods are generally applicable to contamination at depths less than 15 feet. Flooding is a surface application method in which the solution is spread over the land surface in a thin sheet. Flooding is applicable to sites that are flat or gently sloped (i.e., less than 3 percent slope), uniform, without gullies or ridges, and have soils with high hydraulic conductivities (i.e, greater than 10^{-3} cm/sec; such as those found in sands, loamy sands, and sandy loams).

Ponding can be used to increase the infiltration rate of the applied solution above that achieved by flooding. Ponds are constructed by excavating into the ground or by constructing low berms. The depth of the solution in the pond becomes the driving force to increase infiltration rates. Ponding can be used in sandy or loamy soils and in flat areas.

The ditch method of surface spreading utilizes flat-bottomed, shallow, narrow ditches to transport the solution over the land surface; allowing for infiltration of the solution into the ground through both bottom and side surfaces. Gradients in the ditches are kept small to prevent erosion as well as to allow residence time for infiltration. Ditches may be constructed by excavating surface materials or by building small embankments. Ditches are used at sites where it is not desirable to completely cover an entire area with the solution.
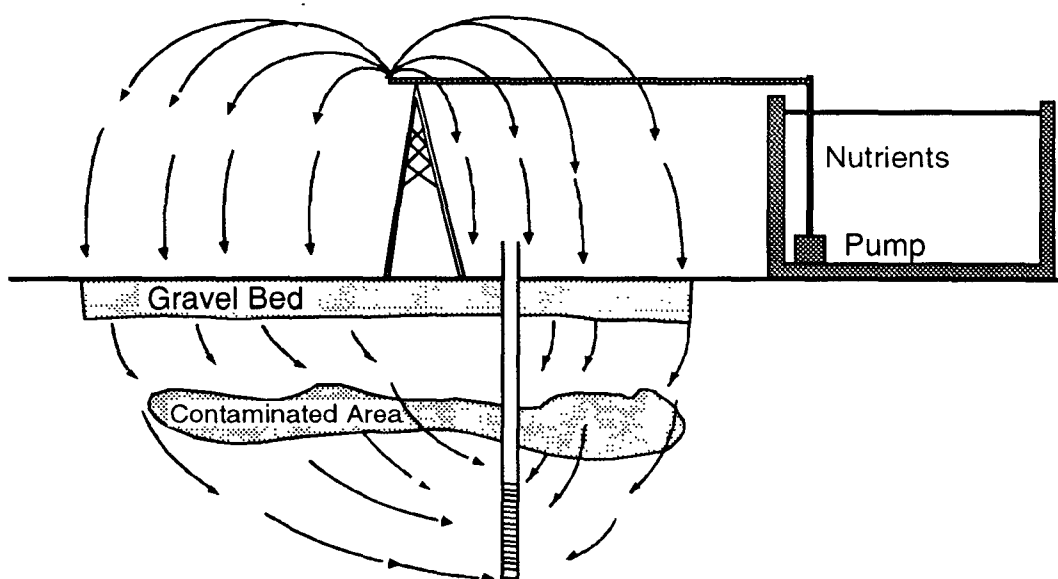

Figure 1. Schematic of a sprinkling system used to deliver nutrients to contaminated subsurface soil.
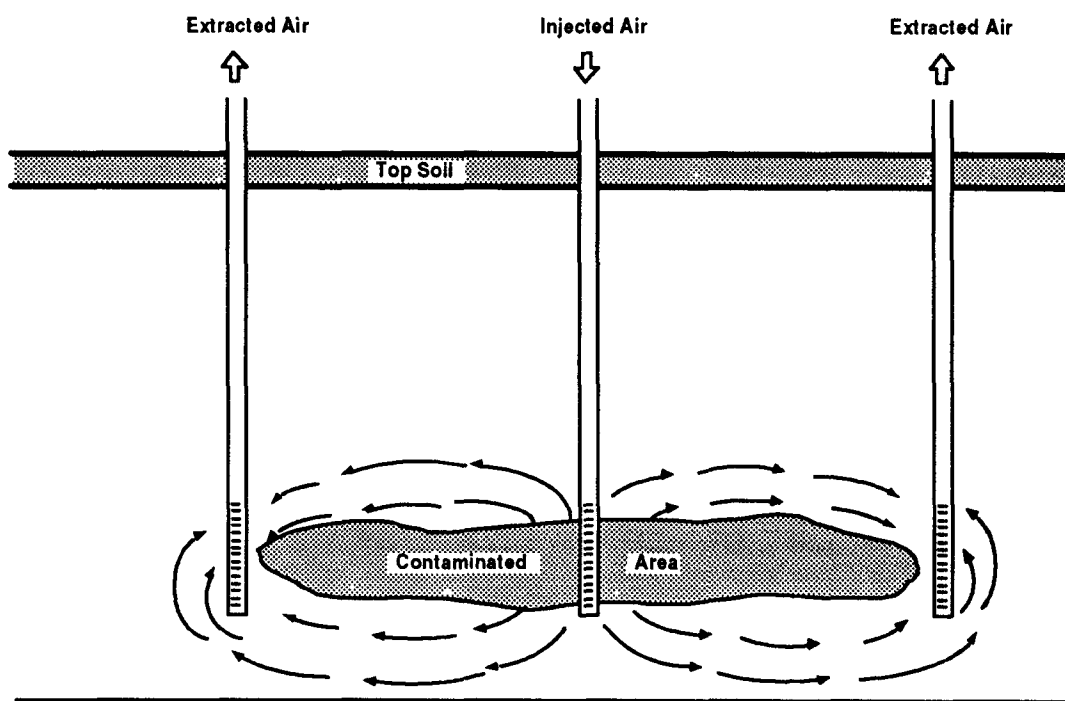
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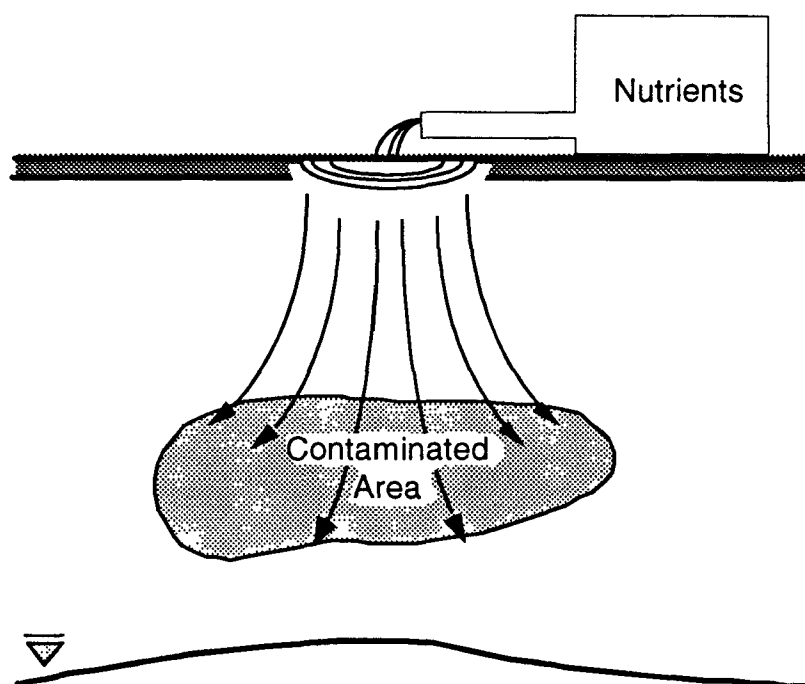Figure 2. Schematic of a bioventing system designed to deliver air to contaminated subsurface soil.

Figure 3. Schematic of a ponding system used to deliver nutrients to contaminated subsurface soil.

Sprinkler systems can be used to deliver solutions uniformly and directly to the ground surface. These systems are less susceptible to topographical constraints than flooding and ponding. Sprinkler systems have been used successfully to deliver nutrients and moisture to bioventing systems where the site was contaminated to a depth of 50 feet (Dupont et al., 1991).

Subsurface gravity delivery systems include infiltration galleries (or trenches) and infiltration beds. These systems are applicable to sites where there is deep contamination or where the surface layers have low permeability. Subsurface systems consist of excavations filled with a porous medium (e.g., coarse sands or gravels) that distribute solutions to the contaminated area. An infiltration gallery consists of a pit or trench that is filled with gravel or stones. The solution fills the pores in the gallery and is distributed to the surrounding soils in both the vertical and horizontal directions. This system is most applicable to sites with sandy or loamy soils. In sites with silty soils, an infiltration gallery can be used but application rates will be reduced. Solutions can be introduced into the gallery by injection at locations along the length of the gallery or through perforated distribution pipe. Infiltration galleries can be used in sites with steep slopes (i.e., up to 25 percent slope) and uneven terrain. Infiltration beds are similar to galleries but are wider and contain more than one perforated distribution pipe. Infiltration occurs almost entirely through the bottom, with little infiltration through sidewall surfaces. This system is applicable to soils with sandy and loamy textures, but limited to sites where the topography is relatively flat (i.e., with less than 5 percent slope) and the terrain is even. Beds can saturate larger areas than a single trench and are easier to install than a multi-trench system.

Forced systems deliver fluids under pressure into a contaminated area through open end or slotted pipes that have been placed to deliver the solution to the zone requiring treatment (Amdurer et al., 1986). These systems are generally applicable to soils with hydraulic conductivities greater than 10^{-4} cm/sec (i.e., fine sandy or coarse silty materials) and high effective porosities (i.e., ranging from 25 to 55 percent). A maximum injection pressure must be established to prevent hydraulic fracturing and uplift in the subsurface, which would cause the fluid to travel upward rather than through the contaminated area. Unlike gravity systems, a forced delivery system is theoretically independent of surface topography and climate.

Design considerations for gravity and forced delivery systems are presented in Amdurer et al. (1986). Application of gravity delivery systems in subsurface bioremediation systems has been demonstrated in bioventing systems (Dupont et al., 1991; Miller et al., 1991). In Russia, methane-oxidizing bacteria grown in fermenters have been injected into lateral core holes in a coal mine (Fliermans and Hazen, 1990). This process has been shown to reduce methane concentration in the air by 50-60 percent in one month, thus reducing the risk of explosions and fire.

Soil Bioventing

Soil bioventing incorporates soil vacuum extraction processes to deliver oxygen to the subsurface to enhance in situ bioremediation of organic contaminants. The large amounts of oxygen-saturated water required for bioremediation often cannot be delivered due to hydraulic conductivity limitations. For example, benzene and hexane, which are common hydrocarbon contaminants, require more than 3 g O_2 per g of hydrocarbon for mineralization. Soil bioventing is applicable to remediation of contaminants of low volatility and can also reduce concentrations of volatile contaminants in off-gases, thus reducing the amount of contaminants requiring off-gas treatment.

To accomplish bioventing, soil vacuum extraction processes are operated at lower than usual air flow rates to reduce vapor extraction quantities and maximize vapor retention times. Soil moisture levels necessary for biological activity are usually higher than those recommended for optimum vacuum extraction operations. The addition of nutrients may also enhance bioremediation. Nutrient addition can be accomplished by surface application, incorporation by tilling into surface soil, and transport to deeper layers through applied irrigation water. Increased soil temperatures have been shown to enhance biodegradation rates in bioventing systems (Miller et al., 1991). Possible means of increasing soil temperature include the use of heated air, heated water, or low-level radio-frequency heating. High temperature should be avoided, since this can result in decreased microbial populations and/or activity.

Soil bioventing has been demonstrated in several field applications (Dupont et al., 1991; Hinchee et al., 1991; Hoeppel et. al., 1991; Miller et al., 1991; van Eyk and Vreeken, 1991; Urlings et al., 1991). At Hill Air Force Base in Utah, a JP-4 jet fuel spill occurred in January 1985 that resulted in the contamination of approximately 0.4 hectares (1 acre) to a depth of approximately 50 feet with approximately 25,000 gallons of JP-4 (Dupont et al., 1991). Soil total petroleum hydrocarbon (TPH) concentrations at the site were as high as 15,000 mg/kg, with average TPH levels of 1,500 mg/kg. Site soil consists of mixed coarse sand and gravel deposits with interspersed, discontinuous clay stringers to a confined ground-water table located approximately 600 feet below ground surface. Prior to initiating a full-scale vacuum extraction project, the fuel tanks were excavated, refurbished, and installed in an above-ground concrete cradle. Excavated soil was placed in a pile and subjected to vacuum extraction.

An SVE system consisting of 15 wells in the undisturbed soil and 10 wells in the excavated soil pile and under the tanks was installed to provide access to the contaminated soil and allow flexibility in the operation of the venting system. The system was operated in a conventional mode to maximize the recovery of volatile components of the JP-4 through volatilization. Venting was initiated on December 18, 1988, at a rate of 1,270 ft^3/hr (approximately 0.04 pore volumes/day),

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and gradually increased to approximately 74,000 ft³/hr (approximately 2.5 pore volumes/day) as the hydrocarbon levels in the vent gas decreased over time. The venting rate during the start-up period was limited by the operating conditions of the catalytic incinerator used to treat the collected vent gas. This high-rate operating mode was maintained from December 18, 1988, through September 15, 1989 with approximately 340 pore volumes (245 x 10⁶ ft³) of soil gas extracted from the site.

In situ respiration tests conducted during the high-rate SVE operating period indicated that significant respiration was occurring without nutrient or moisture addition, and that enhancement of biodegradation might be possible under modified site management conditions. Biodegradation was a significant removal mechanism during the initial high-rate venting, accounting for 15 to 25 percent of the recovered hydrocarbon. To assess the potential for enhancing biodegradation rates, a series of laboratory and field biotreatability studies were conducted to evaluate moisture and nutrient additions. The effect of SVE system operational parameters on biodegradation rates was also evaluated by decreasing air flow rates and increasing flow path length.

A number of in situ respiration tests were conducted during the field studies to assess the impact of different engineering management options on microbial activity. A total of three tests were conducted to monitor the effect of different management approaches,including: (1) flow rate and operating configuration modifications , (2) moisture addition, and (3) moisture and nutrient addition. Biodegradation reactions were estimated based on cumulative oxygen consumption and carbon dioxide production. All biodegradation calculations were normalized to background CO_2 and O_2 concentrations so that the effects of field management techniques could be isolated from changes in background respiration taking place during the study.

The results of these studies indicated that moisture addition and operational modifications significantly enhanced biodegradation rates. Based on analyses of O_2 uptake rates, moisture addition (35% to 50% field capacity) was shown to statistically accelerate in situ respiration at the site. However, nutrient addition generally did not statistically increase the degradation rates of residual JP-4 constituents. The operational modifications (reduced air flow rate, increased path length) significantly improved biodegradation rates. Fuel removal due to biodegradation increased to greater than 80 percent, resulting in an additional 12,000 lb of total petroleum hydrocarbons being degraded during the bioventing portion of the study. Initial hydrocarbon (on a carbon equivalent basis) removal rates of 70 lb/day were maintained at an average rate of greater than 100 lb/day following system operating modifications.

Soil bioventing was also investigated at Tyndall Air Force Base in Florida to remediate sandy soils contaminated by past jet fuel storage activities (Miller, 1990; Miller et al., 1991). Hydrocarbon concentrations in the soil ranged from 30 to 23,000 mg/kg. The contaminated area was dewatered

prior to system installation. The impact of moisture and nutrient addition was investigated during a 7-month period. Moisture addition had no significant effect on biodegradation rate in this system. Nutrient addition also did not affect biodegradation rate, since naturally occurring nutrients were present in adequate quantities to support the amount of biodegradation observed. Biodegradation rates were shown to be affected by soil temperature and followed predicted rates based on the van't Hoff-Arrhenius equation. Fifty-five percent removal was attributed to biodegradation during the period of study, but a series of flow rate tests showed that biodegradation could be increased to 85 percent by decreasing air flow rates. The optimal air flow conditions were found to be the removal of 0.5 air flow volumes per day. The contaminated gas phase was drawn through clean soil to increase gas residence time within the soil. This augmented in situ biodegradation and eliminated the need for off-gas treatment as well as reducing exposure to off-gas.

Research: Hydraulic Fracturing, Radial Drilling

Research areas are focusing on methods to increase the capacity of current systems to deliver increased concentrations of required solutions to the subsurface. Two of these systems are discussed below.

Hydraulic fracturing

Hydraulic fracturing is a technique that involves using hydraulic pressure to induce cracking in rock or clay/silt lenses in the vicinity of a borehole, which develops a larger framework of interconnected pore space. The newly created pore space is filled with solid, granular materials, which can act as permeable channels to increase the rate and area of delivery of fluids containing nutrients or oxygen to the subsurface (Murdoch et al., 1990; Murdoch et al., 1991; Davis-Hoover et al., 1991). The hydraulic fractures may be filled with granules of slow-dissolving nutrients or oxygen-releasing chemicals, which may provide a reservoir of these compounds for the enhancement of bioremediation. This technique could also potentially be used in recovery systems, e.g., by increasing extraction of vapor phases in soils with low permeabilities, or by forming horizontal sheet-like drains to capture leachates in soil flushing systems.

Hydraulic fracturing has been successfully utilized in petroleum engineering in many types of geologic materials, ranging from granite to poorly consolidated sediments. For remedial applications, it has been demonstrated in soft clay soils at shallow depths, but has not yet been demonstrated in a wide range of soils or at waste sites. For use in remedial applications, hydraulic fracturing has been classified by the U.S. EPA as an emerging technology (i.e., research on its use is in progress) (Murdoch et al., 1990).

Radial drilling

Radial well technology consists of drilling horizontal wells radially outward from a central borehole. This enhances access to a contaminated subsurface environment by

increasing the volume serviced by each vertical well (Murdoch et al., 1990). Radial wells can be placed at the same level or on multiple levels in the same borehole. The use of horizontal wells allows access to fracture zones that are perpendicular to the ground surface and allows contaminated areas to be entered laterally rather than vertically.

Radial wells have been installed in both consolidated rock and unconsolidated materials (Murdoch et al., 1990). In unconsolidated formations, drilling rates range from 5 to 120 ft/min, while in very hard, homogeneous basalt, rates range from 0.10 to 0.50 ft/min. For use in remedial applications, radial well drilling has been classified by the U.S. EPA as an emerging technology (i.e., research on its use is in progress) (Murdoch et al., 1990).

Waste, Soil, and Site Information Requirements for Evaluation and Management of In Situ Bioremediation

Adequate site characterization including: surface and subsurface soil characteristics, hydrogeology, and microbiological characteristics, serve as the basis for rational design of any subsurface soil bioremediation system. A thorough site characterization is necessary to determine both the three-dimensional extent of contamination as well as engineering and management constraints which may limit the rate and extent of remediation. Specific characterization information regarding waste, soil, and hydrogeology is required in order to assess the potential effectiveness of bioremediation. Specific waste characterization information required includes the relative aerobic biodegradability of waste chemicals under optimum conditions. Important hydraulic, physical, and chemical properties of soils that affect the behavior of organic constituents in the vadose zone are presented in Sims et al. (1989). Subsurface soil characterization information required includes identification of limiting soil environmental factors identified in Table 1. Required site characterization information includes identification of potential limiting factors with regard to relative ease of delivery and recovery listed in Table 2.

Based upon waste, subsurface soil, and site characterization information, appropriate containment strategies need to be considered for the mobile contaminant phases associated with the subsurface (Figure 1). Naturally occurring containment may be sufficient with regard to preventing escape of mobile phases under existing site conditions. However, other containment strategies may need to be considered if materials are to be added or removed from the subsurface to stimulate microbial activity. These may include volatiles removed in vacuum extraction, water used to add oxygen and nutrients, or NAPLs if soil flushing is carried out.

For each chemical (or chemical class), the information required is summarized as: (1) characteristics related to potential leaching, e.g., water solubility, octanol/water partition coefficient, solid sorption coefficient; (2) volatilization, e.g., vapor pressure, relative volatilization index;

(3) Henry's Law Constant ; (4) potential biodegradation, e.g., half-life, degradation rate, biodegradability index; and (5) chemical reactivity, e.g., hydrolysis half-life, soil redox potential (Sims et al., 1984; Sims et al., 1989).

Information from waste and site characterization studies, and laboratory evaluations of biodegradation may be integrated by using appropriate mathematical models to predict: (1) the potential for bioremediation of and (2) the potential for cross-contaminating other media (i.e., ground water under the contaminated area, atmosphere over the site or at the site boundaries, surface waters, etc). The models used will be highly dependent on site characteristics and contaminants of interest. These may range from "back-of-the-envelope" calculations to sophisticated fate and transport computer models.

Mass Balance Approach to In Situ Subsurface Bioremediation

Successful subsurface bioremediation depends upon thorough characterization and management of each subsurface phase with regard to containment, stimulation of microbial activity, and monitoring strategies. The chemical mass balance approach provides a framework for evaluating, managing, and monitoring subsurface soil bioremediation (Sims, 1990). Mass balance helps obtain specific information that is needed to determine fate and behavior, evaluate and select management options for in situ bioremediation, and monitor treatment effectiveness for specific chemicals in specific subsurface phases. The information needed to construct a mass balance for subsurface contamination simultaneously addresses site characterization and biodegradation rates.

A necessary first step in mass balance requires characterizing each phase present in the subsurface (Figure 1) with regard to location, amount, and heterogeneity of the subsurface environment to assess which chemicals are associated with which phase(s). This information allows determination of the relative bioavailability of chemicals. For example, chemicals associated with aqueous and gas phases are generally more bioavailable than chemicals associated with solid and NAPL phases. In addition, chemicals associated with aqueous and gas phases are more prone to migration. This information also allows determination of the need for containment by defining where contamination is migrating under the influence of natural processes. The problem can be defined in the context of mobility versus biodegradation for chemicals. Is the rate of biodegradation (either natural or enhanced) such that chemicals which are prone to leaching or volatilization degrade before either occurs? Using mathematical models or other tools, chemicals can be ranked in order of their relative tendencies to leach, volatilize, or remain in-place under subsurface site-specific conditions. Containment and management options can then be selected that address specific escape and attenuation pathways. For example, SVE may be appropriate as a managerial tool to remove highly volatile, biologically recalcitrant chemicals from soil before switching

to a bioventing mode to remove less volatile, easily biodegraded compounds. Specific waste phases may be addressed at specific times during bioremediation. Finally, comprehensive monitoring programs can be designed to track specific chemicals in specific phases in the subsurface at specific times.

After a phase is contained through natural or managed processes, techniques to enhance microbial activity may be applied. Monitoring strategies can then be designed to ensure that the rate and extent of biodegradation within each phase, as well as transfer of chemicals between phases, are measured. Biodegradation rates of organic compounds in soil systems are generally measured by monitoring their disappearance in a soil through time. Rates of degradation are often expressed as a function of the concentration of one or more of the constituents being degraded. This is accomplished by measuring at specific time intervals the concentration of contaminants of interest (in the medium of interest, i.e., soil phase, gas phase, etc.), through a properly designed sampling and analysis plan. This sampling and analysis plan should be statistically valid and provide sufficient information to determine the rate of disappearance of contaminants of interest or appropriate surrogates, such as petroleum hydrocarbons (TPH). Care should be taken to ensure that transfer or partitioning of contaminants from one phase to another is not misinterpreted as biodegradation within the source phase. Abiotic losses such as volatilization and leaching must be defined in order to accurately determine biodegradation rates. Identification of metabolic transformation products is also necessary since metabolites may be more mobile or toxic than the parent compounds. In addition, measuring only for parent compounds and not metabolites may tremendously overestimate extent of biodegradation. In addition, identification of metabolites is warranted when known daughter products are toxic.

Recommendations

There is currently a lack of information concerning some aspects of in situ bioremediation of subsurface soils. Specific areas where additional information is required include site characterization with regard to effects of physical, chemical, and hydrologic properties on microbial distribution, numbers, and activity. Field research to obtain these types of information is currently limited; however, this information is required in order to estimate the feasibility of bioremediation for subsurface contamination. Implementation of subsurface remediation is currently limited to a significant extent by the difficulty of establishing adequate systems for delivery and recovery of chemicals for augmenting biological activity. As research continues, these difficulties may be overcome as more information becomes available concerning the applicability of innovative technologies in the remediaiton of contaminated soil.

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